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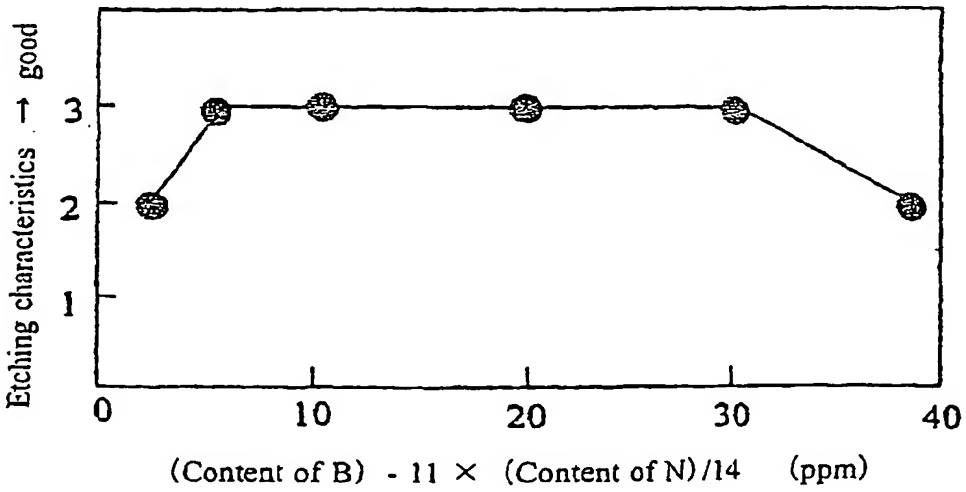
(54) MATERIAL FOR SHADOW MASK, METHOD FOR PRODUCTION THEREOF, SHADOW MASK AND IMAGE RECEIVING TUBE

(57) A material for a shadow mask having the following composition of components: C ≤0.0008 wt%, Si ≤ 0.03 wt%, Mn: 0.1 to 0.5 wt%, P ≤ 0.02 wt%, S ≤ 0.02 wt%, Al: 0.01 to 0.07 wt%, N ≤ 0.0030 wt%, B: an amount satisfying the formula: 5 ppm ≤ B-11/14 × N ≤ 30 ppm, balance: Fe and inevitable impurities; a method for producing the material; a shadow mask using the material (cold rolled steel sheet); and an image receiving tube equipped with the shadow mask. The material has excellent etching characteristics, which are uniform within the same coil, and excellent press formability.

Fig. 1



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Description

TECHNICAL FIELD

[0001] The present invention relates to a cold rolled steel sheet used as shadow mask material for a color picture tube, a method for manufacturing the cold rolled steel sheet, a shadow mask utilizing the cold rolled steel sheet and a picture tube with the shadow mask.

BACKGROUND OF THE INVENTION

[0002] A cold rolled steel sheet used for shadow mask material has been manufactured by the following manufacture steps. That is, low carbon steel manufactured by a steel maker is made by pickling and cold rolling so as to form a steel sheet having a predetermined thickness. After degreasing, the steel sheet is decarbonized and annealed in a wet atmosphere in a box-type anneal furnace. Then, the steel sheet is secondary cold rolled so as to form a cold rolled steel sheet with a final thickness.

[0003] The cold rolled steel sheet manufactured by such a method is installed in a picture tube after having been made by photo etching, annealing, pressing and baking. Unless carbon originally contained in the cold rolled steel sheet is decarbonized sufficiently during the above described steps, improper etching and improper press forming would result. Therefore, the content ratio of decarbonized and annealed carbon should be equal or less than 0.0015 wt%, preferably equal or less than 0.0008 wt%.

[0004] Regarding a cold rolled steel sheet used for a shadow mask manufactured by a method comprising the above described etching and press forming steps, it has been required that etching performance and press forming performance should be more stable than the conventional ones since a picture tube is required to provide high picture quality and improve its fine degree.

[0005] Japanese Patent Laid-open Publication No. Sho 56-139624, No. Hei 2-61029 and No. Hei 8-269627 disclose a method to solve such a problem, respectively. In the above prior art, although steel components and annealing condition are described, these are not sufficient to provide stable etching performance and press forming performance in order to satisfy recent requirements with respect to the shadow mask material such as high picture quality and its fine improvement.

[0006] An object of the invention is to resolve the above described drawbacks in the prior art and to provide a shadow mask material with excellent uniform etching characteristics in a coil and press forming characteristics installed in a picture tube.

DISCLOSURE OF THE INVENTION

[0007] Shadow mask material according to the present invention is characterized in that it comprises nitrogen equal or less than 0.0030 wt%, boron satisfying an inequality of $5 \text{ ppm} \leq \text{B-11/14} \times \text{N} \leq 30$ ppm and the residue including iron and unavoidable impurities.

[0008] Shadow mask material according to the present invention is characterized in that it comprises carbon equal or less than 0.0008 wt%, silicon equal or less than 0.03 wt%, manganese from 0.1 to 0.5 wt%, phosphorus equal or less than 0.02 wt%, sulfur equal or less than 0.02 wt%, aluminum from 0.01 to 0.07 wt%, nitrogen equal or less than 0.0030 wt% and boron satisfying an inequality of $5 \text{ ppm} \leq \text{B-11/14} \times \text{N} \leq 30$ ppm and the residue including iron and unavoidable impurities.

[0009] A method for manufacturing shadow mask material made of a steel sheet according to the present invention is characterized in that it comprises nitrogen equal or less than 0.0030 wt%, boron satisfying an inequality of $5 \text{ ppm} \leq \text{B-11/14} \times \text{N} \leq 30$ ppm and the residue including iron and unavoidable impurities, wherein a final hot rolling temperature is higher than a point Ar_3, the steel sheet is hot rolled at a coiling temperature from 540 to 680°C and cold rolled after pickling and then the steel sheet is annealed in a continuous annealing step so as to control a content ratio of residual carbon equal or less than 0.0008 wt%.

[0010] A method for manufacturing shadow mask material made of a steel sheet according to the present invention is characterized in that it comprises carbon equal or less than 0.0008 wt%, silicon equal or less than 0.03 wt%, manganese from 0.1 to 0.5 wt%, phosphorus equal or less than 0.02 wt%, sulfur equal or less than 0.02 wt%, aluminum from 0.01 to 0.07 wt%, nitrogen equal or less than 0.0030 wt% and boron satisfying an inequality of $5 \text{ ppm} \leq \text{B-11/14} \times \text{N} \leq 30$ ppm and the residue including iron and unavoidable impurities, wherein a final hot rolling temperature is higher than a point Ar_3, said steel sheet is hot rolled at a coiling temperature from 540 to 680°C and cold rolled after pickling and then said steel sheet is annealed in a continuous annealing step so as to control a content ratio of residual carbon equal or less than 0.0008 wt%.

[0011] A shadow mask according to the present invention is characterized in that it comprises the above described

shadow mask material.

[0012] A picture tube according to the present invention is characterized in that it comprises the above described shadow mask.

BRIEF DESCRIPTION OF THE DRAWING

[0013] Fig. 1 is a graph for showing a relation of an etching characteristic and an inequality of amounts of boron and nitrogen.

BEST MODE FOR CARRYING OUT THE INVENTION

[0014] Regarding chemical composition of the hot rolled steel sheet, the following chemical composition is preferable. That is, a steel sheet which comprises nitrogen equal or less than 0.0030 wt%, boron satisfying an inequality of 5 ppm ≤ B-11/14 × N ≤ 30 ppm and the residue including iron and unavoidable impurities.

N: < 0.0030 wt%

[0015] Nitrogen in steel makes nitride with aluminum. On the other hand, the aging effect of the steel is reduced by decreasing solid soluble nitrogen. Therefore, it is preferable that the amount of nitrogen is as small as possible. In order to maintain the press forming characteristics as shadow mask material, it is necessary that the amount of nitrogen is remarkably low and it is preferable that the upper limit is 0.0030 wt%, more preferably 0.0020 wt%.

Boron: 5 ppm ≤ B-11/14 × N ≤ 30 ppm

[0016] Boron in steel makes crystal grains in a thin steel sheet more uniform so that excellent etching characteristics can be obtained as shadow mask material. Particularly, boron is very effective with respect to an extremely thin shadow mask having a thickness of 0.1 to 0.2 mm which has been used recently.

[0017] It is preferable that boron is added to steel since boron is an effective element so as to fix solid soluble nitrogen. On the other hand, if the amount of boron is too high, crystal grains are extremely fine and its magnetic characteristics are influenced detrimentally. Therefore, it is preferable that the amount of boron is within a predetermined range.

[0018] In the present invention, it is preferable that the content of boron satisfies the above inequality. If the content ratios of nitrogen and boron are within the above described ranges, respectively, excellent etching characteristics can be obtained as shown in Fig. 1. Further, in the present invention, it is preferable that the following chemical composition of the hot rolled steel sheet is controlled to obtain a steel sheet suitable for an extremely thin shadow mask material having a thickness of 0.08 to 0.2 mm.

[0019] That is, the content of carbon is equal or less than 0.0030 wt%, the content of silicon is equal or less than 0.03 wt%, the content of manganese is from 0.1 to 0.5 wt%, the content ratio of phosphorus is equal or less than 0.02 wt%, the content ratio of sulfur is equal or less than 0.02 wt% and the content ratio of aluminum is from 0.01 to 0.07 wt%. The reason of the above ratios will be described hereinafter.

Carbon: ≤ 0.0030 wt%

[0020] The amount of carbon in hot rolled steel sheet is much influenced by a continuous annealing step for decarbonizing. If the content ratio of carbon exceeds 0.0030 wt%, carbon can not be decarbonized sufficiently in the continuous annealing step. To provide a shadow mask material in which the content ratio of carbon is equal or less than 0.0008 wt%, the annealing temperature has to be increased and the annealing time has to be extended. Therefore, the manufacturing cost would become higher and productivity would become lower. It is preferable that the upper limit is 0.0030 wt%, more preferably 0.0020 wt%.

Silicon: ≤ 0.03 wt%

[0021] Silicon contained in shadow mask material is an element to prevent shadow mask material from blackening in a blackening treatment for manufacturing a picture tube. Although the content ratio is preferable as small as possible, silicon is an unavoidable element in an aluminum killed steel. It is preferable that the upper limit is 0.03 wt%, more preferably 0.02 wt%.

Manganese: 0.1 to 0.5 wt%

[0022] Manganese is necessary to prevent sulfur as an impurity from imparting hot brittleness to a hot rolled steel in a hot rolling step. In the case of an extremely thin shadow mask material according to the present invention, the material is apt to crack in a cold rolling step. Therefore, it is preferable to add a predetermined amount of manganese. The content ratio of manganese is preferably equal or more than 0.1 wt%, more preferably equal or more than 0.2 wt%, and further more preferably equal or more than 0.25 wt%.

[0023] On the other hand, the upper limit of the content ratio of manganese is preferably 0.5 wt%, more preferably 0.4 wt% and further more preferably 0.35 wt%, since the forming characteristics are deteriorated if the content ratio exceeds 0.6 wt%.

Phosphorus: ≤ 0.02 wt%

[0024] In the shadow mask material, phosphorus reduces the size of crystal grains so that the magnetic characteristics become worse. It is preferable that the content ratio of phosphorus is as small as possible. Particularly, in such extremely thin shadow mask material according to the present invention, phosphorus has a very detrimental influence, the content ratio of phosphorus is preferably equal or less than 0.02 wt%.

Sulfur: ≤ 0.02 wt%

[0025] In hot rolled steel, sulfur is an unavoidable element and impurity which imparts hot brittleness to the steel. It is very preferable that the content ratio of sulfur is as small as possible. Particularly, in such extremely thin shadow mask material according to the present invention, the material is apt to crack in a cold rolling step. Therefore, it is preferable to avoid sulfur as much as possible. To avoid the above phenomenon, the upper limit is preferably 0.02 wt%, more preferably 0.015 wt% and further more preferably 0.01 wt%.

Aluminum: 0.01 to 0.07 wt%

[0026] In the step of manufacturing hot rolled steel, aluminum is added to molten steel as a deoxidizer and then removed as slag. Unless the added amount of aluminum is sufficient, a certain deoxidization effect can not be obtained. It is preferable that aluminum is added affirmatively so as to form aluminum nitride in the hot rolling step and the annealing step and to prevent solid soluble nitrogen from aging by fixing nitrogen. Particularly, in the case of the extremely thin shadow mask material according to the present invention, the material is apt to crack caused by including impurity such as oxide in a cold rolling step. Therefore, it is necessary to add aluminum as much as possible. The lower limit is preferably 0.01 wt%, more preferably 0.02 wt%.

[0027] On the other hand, even if the content ratio of aluminum exceeds 0.07 wt%, the above effect can not be improved so much. Such redundant aluminum tends to increase the recrystallization temperature and to increase the amounts of the inclusion. The upper limit is preferably 0.07 wt%, more preferably 0.05 wt%, further more preferably 0.04 wt%.

[0028] Residue: Iron and avoidable elements without influencing the etching characteristics and the press forming characteristics are not restricted.

[0029] A method for manufacturing the extremely thin shadow mask material according to the present invention will be described. Although the slab heating temperature and the hot rolling conditions are not so restricted in the present invention, the slab heating temperature is preferably higher than 1100°C so as to keep the hot rolling temperature since the hot rolling property becomes worse if the slab heating temperature is less than 1100°C. On the other hand, if the slab heating temperature is too high, nitride will be dissolved and become solid soluble again. The slab heating temperature is preferably less than 1220°C.

[0030] If the final hot rolling temperature is equal or less than Ar_3, crystal grains are mixed and become large in crystal structure of the hot rolled steel sheet so that the etching characteristics and the press forming characteristics are deteriorated. The final hot rolling temperature is preferably higher than Ar_3.

[0031] A lower limit of the coiling temperature is preferably 540°C from the point of quality stability of the hot rolled steel sheet along a width direction and a longitudinal direction of a coil in a hot rolling step. On the other hand, if the coiling temperature exceeds 680°C, descaling characteristics are deteriorated. The coiling temperature is preferably from 540°C to 680°C.

Pickling, first cold rolling step

[0032] Pickling and first cold rolling step may be conducted under normal conditions. In order to decarbonize and

anneal an extremely thin shadow mask material according to the present invention effectively, the thickness of the steel sheet after the first cold rolling is preferably equal or less than 0.6 mm and more preferably equal or less than 0.5 mm.

Continuous annealing step

[0033] A continuous annealing step is an important step in the present invention. The continuous annealing step is preferably operated in a condition wherein the sheet temperature is equal or more than 750°C, the soaking period is equal or more than 60 seconds, the content ratio of hydrogen is from 0 to 75 % and the residue is nitrogen gas in the annealing atmosphere and the dew point is from -30°C to 70°C.

Annealing temperature

[0034] The annealing temperature influences the decarbonization effect and the etching characteristics. If the annealing temperature is less than 750°C, it takes long time to decarbonize. In addition to reduce the productivity, a structure of recrystallization after annealing becomes uneven so that uniform etching characteristics can not be obtained. Accordingly, the annealing temperature is preferably equal or higher than 750°C.

Annealing time

[0035] The annealing time is preferably equal or more than 60 seconds. If the annealing time is less than 60 seconds, the decarbonization with respect to the extremely thin shadow mask material is insufficient so that the content of carbon can not be reduced to a target level equal or less than 0.0008 %. Although the upper limit is not necessary restricted, the annealing time is preferably equal or less than 120 seconds from a point of the productivity and an avoidance of large grains.

Hydrogen density and dew point in a continuous annealing atmosphere

[0036] If the content ratio of hydrogen gas in the continuous annealing atmosphere can be maintained equal or less than 70 %, a content ratio of carbon in the extremely thin shadow mask material can be reduced to a level equal or less than 0.0008 %. Even if the content ratio of hydrogen gas exceeds 70 %, the decarbonization time is not so changed and the manufacturing cost is increased. The upper limit of the content ratio of hydrogen gas is preferably 70 %. In the case that the dew point is in a range from -30°C to 70°C, the content ratio of carbon in the extremely thin shadow mask material is equal or less than 0.0008 %.

Secondary cold rolling after annealing

[0037] The reduction ratio of secondary cold rolling after annealing is preferably from 41 % to 90 % so as to provide the necessary strength for the extremely thin shadow mask material. If the reduction ratio is equal or less than 40 %, the necessary strength can not be obtained. If the rolling ratio is equal or more than 91 %, the number of rolling steps is increased and the productivity is reduced. Therefore, the upper limit is preferably 90 %. Through the secondary cold rolling, the final thickness of the extremely thin shadow mask material becomes from 0.1 to 0.2 mm.

EXAMPLES

[0038] The examples according to the present invention will be described below. Steel sheet having a chemical composition as shown in Table 1 is hot rolled so as to form a hot rolled steel sheet having a thickness of 2.3 mm. After pickling, the steel sheet is cold rolled so as to form a cold rolled steel sheet having a thickness of 0.3 mm. During a continuous annealing step, decarbonization annealing is operated under various conditions. Table 2 shows the annealing conditions and the content ratio of carbon after annealing with respect to each example. Further, the extremely thin shadow mask material having a thickness of 0.1 mm is formed by the cold rolling.

Table 1

Steel sheet no.	Chemical composition (wt%)								
	C	Si	Mn	P	S	Al	N	B	Fe
1	0.0021	0.03	0.36	0.017	0.017	0.041	0.0017	0.0021	Residue

Table 1 (continued)

Steel sheet no.	Chemical composition (wt%)								
	C	Si	Mn	P	S	Al	N	B	Fe
2	0.0021	0.02	0.22	0.017	0.018	0.045	0.0023	0.0030	Residue
3	0.0024	0.02	0.30	0.010	0.016	0.048	0.0021	0.0021	Residue
4	0.0018	0.03	0.33	0.013	0.012	0.051	0.0010	0.0013	Residue

Table 2

Example or comparative example	Steel sheet no.	Annealing temperature (°C)	Annealing time (second)	Content ratio of hydrogen gas (%)	Wet point (°C)	Carbon content ratio in steel after annealing
Example 1	1	760	60	5	20	0.0007
Example 2	1	775	60	5	20	0.0006
Example 3	1	800	60	50	-30	0.0005
Example 4	2	775	60	5	20	0.0006
Example 5	3	775	60	5	20	0.0006
Example 6	4	775	60	5	20	0.0006
Comparative example 1	1	725	80	5	20	0.0011
Comparative example 2	1	760	30	5	20	0.0014
Comparative example 3	1	760	60	5	-40	0.0010

[0039] In the following, a shadow mask used with the above described material will be described. Water soluble casein-resist is coated on both surfaces of the shadow mask material. Then, dried resist coated on both surfaces is patterned by a pair of dry plates on which ins and outs patterns are drawn. After patterning, exposure treatment, film hardening treatment and baking treatment are operated. Then, ferric chloride solution (solution temperature 60°C, specific gravity 48° Be) is sprayed on both patterned resist surfaces as an etching solution so as to etch the shadow mask material. After etching, the steel sheet is cleaned with an alkaline solution so as to peel the resist. Finally, the shadow mask is manufactured by cleaning and drying. The result of the evaluation of the etching characteristics is shown in Fig. 1. In Fig. 1, the vertical axis indicates etching characteristics and the horizontal axis indicates the relation between the amounts of boron and nitrogen. Judging from Fig. 1, excellent etching characteristics can be obtained if the relation between the amount of boron and nitrogen satisfies the inequality of $5 \text{ ppm} \leq B - 11/14 \times N \leq 30 \text{ ppm}$.

[0040] In Fig. 1, the etching characteristics are evaluated by a three ranked standard depending on the shape of an etched hole.

[0041] Evaluation point 3 --- good: the profile of the slot hole in view from an etching surface does not have any practical problems.

[0042] Evaluation point 2 --- intermediate: the profile of the slot hole in view from an etching surface is a little uneven.

[0043] Evaluation point 1 --- poor: the profile of the slot hole in view from an etching surface is deformed.

[0044] In the following, a condition in which the shadow mask according to the present invention is attached to a frame will be described. The shadow mask according to the present invention is fixed on the frame while tensile force is loaded. Although various methods for fixing a shadow mask on a frame can be considered, a welding method is the best known method. Initially, while a center portion of each upper and lower frame bars of a frame is forcibly flexed toward an inward direction, a shadow mask is fixed on the frame. Then, flexed upper and lower frame portions are returned to original positions, respectively (releasing forcibly applied force) so that tensile force can be applied to the shadow mask along an upper-lower direction.

[0045] When the shadow mask is fixed on the frame as described above, it is preferable that tensile force along a right-left direction of which amount is less than the tensile force along the upper-lower direction is loaded. In a picture

tube according to the present invention, it is preferable that strong tensile force is applied along the upper-lower direction. In addition to the load in the upper-lower direction, the tensile force is loaded in the right-left direction. Thus the shadow mask can prevent from crinkling by applying the tensile force along the upper-lower direction. However, if the large amount of tensile force was applied on the shadow mask along the right-left direction, slot holes formed on the shadow mask would be deformed.

POSSIBILITY OF USE OF THE INVENTION

[0046] Unless the carbon amount is decarbonized sufficiently, etching becomes uneven in an etching step for manufacturing a shadow mask. Thereby, the profile of etched holes does not become uneven and unevenness of the surface become large. Unless the carbon amount is equal or less than 0.0008%, sufficient etching characteristics can not be obtained. If the carbon content is too high, the shadow mask material becomes hard and shape freezing characteristics are deteriorated in a press forming step. Therefore, the carbon amount should be lowered.

[0047] As shown in Fig. 1, boron can fix nitrogen and prevent nitrogen from occurring stretcher strain caused by aging solid soluble nitrogen and uniform recrystallized grains. In order to stabilize the etching characteristics, the necessary amount of boron must be added to the material. However, if the added amount of boron is too large, crystal grains become extremely fine so that the high quality and the magnetic characteristics are deteriorated.

Claims

1. Shadow mask material comprising nitrogen equal or less than 0.0030 wt%, boron satisfying an inequality of 5 ppm $\leq$ B-11/14 $\times$ N $\leq$ 30 ppm and the residue including iron and unavoidable impurities.

2. Shadow mask material comprising carbon equal or less than 0.0008 wt%, silicon equal or less than 0.03 wt%, manganese from 0.1 to 0.5 wt%, phosphorus equal or less than 0.02 wt%, sulfur equal or less than 0.02 wt%, aluminum from 0.01 to 0.07 wt%, nitrogen equal or less than 0.0030 wt% and boron satisfying an inequality of 5 ppm $\leq$ B-11/14 $\times$ N $\leq$ 30 ppm and the residue including iron and unavoidable impurities.

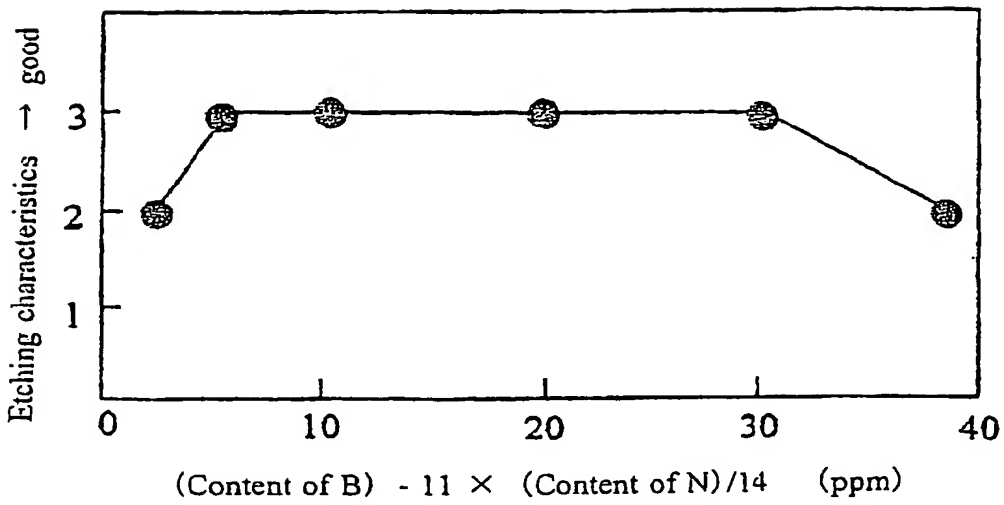
3. A method for manufacturing shadow mask material made of a steel sheet **characterized in that** it comprises nitrogen equal or less than 0.0030 wt%, boron satisfying an inequality of 5 ppm $\leq$ B-11/14 $\times$ N $\leq$ 30 ppm and the residue including iron and unavoidable impurities, wherein the final hot rolling temperature is higher than a point Ar_3, said steel sheet is hot rolled at a coiling temperature from 540 to 680°C and cold rolled after pickling and then said steel sheet is annealed in a continuous annealing step so as to control the content ratio of residual carbon to equal or less than 0.0008 wt%.

4. A method for manufacturing shadow mask material made of a steel sheet **characterized in that** it comprises carbon equal or less than 0.0008 wt%, silicon equal or less than 0.03 wt%, manganese from 0.1 to 0.5 wt%, phosphorus equal or less than 0.02 wt%, sulfur equal or less than 0.02 wt%, aluminum from 0.01 to 0.07 wt%, nitrogen equal or less than 0.0030 wt% and boron satisfying an inequality of 5 ppm $\leq$ B-11/14 $\times$ N $\leq$ 30 ppm and the residue including iron and unavoidable impurities, wherein the final hot rolling temperature is higher than a point Ar_3, said steel sheet is hot rolled at a coiling temperature from 540 to 680°C and cold rolled after pickling and then said steel sheet is annealed in a continuous annealing step so as to control the content ratio of residual carbon to equal or less than 0.0008 wt%.

5. A shadow mask made of the material as claimed in claim 1 or claim 2.

6. A picture tube with said shadow mask as claimed in claim 5.

Fig. 1



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP00/01402

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl[7] C22C 38/00, 38/06, C21D 9/46, H01J 9/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl[7] C22C 38/00, 38/06, C21D 9/46, H01J 9/14

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2000
Kokai Jitsuyo Shinan Koho 1971-2000 Jitsuyo Shinan Toroku Koho 1996-2000

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DERWNT WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP, 2-254139, A (Toyo Kohan Co., Ltd.), 12 October, 1990 (12.10.90) (Family: none)	1,5,6 1-6
Y	JP, 8-269627, A (Kawasaki Steel Corporation), 15 October, 1996 (15.10.96) (Family: none)	1-6
Y	JP, 1-136933, A (Nippon Steel Corporation), 30 May, 1989 (30.05.89) (Family: none)	1-6

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
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Date of the actual completion of the international search	Date of mailing of the international search report
06 June, 2000 (06.06.00)	20 June, 2000 (20.06.00)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
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